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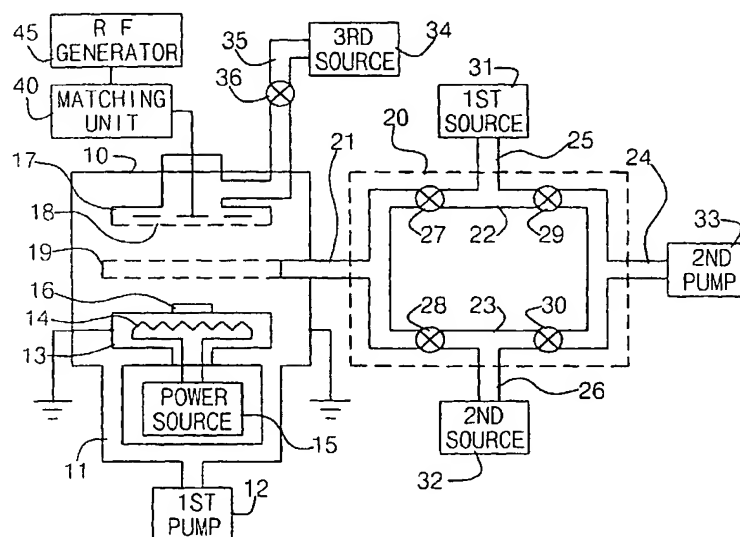
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(54) Title: **AUTOMATIC VALVE CONTROL SYSTEM IN PLASMA CHEMICAL VAPOR DEPOSITION SYSTEM AND CHEMICAL VAPOR DEPOSITION SYSTEM FOR DEPOSITION OF NANO-SCALE MULTILAYER FILM**



(57) Abstract: An automatic valve control system in PCVD system or CVD system for deposition of nano-scale multilayer film having nano-scale ultra-high hardness and multifunction is provided. The automatic valve control system includes a chamber in which a multilayer thin-film can be formed of at least two components by using PCVD method or CVD method, at least two source supplies supplying a reaction material, at least two paths each whose middle portion is connected to each source supply, whose one end is connected to the chamber, and whose other end is connected to a bypass tube, a vacuum pump connected to the bypass tube, and at least four valves installed in either side of each path around each connection portion in each source supply, which is opened or closed.

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**AUTOMATIC VALVE CONTROL SYSTEM IN PLASMA CHEMICAL VAPOR
DEPOSITION SYSTEM AND CHEMICAL VAPOR DEPOSITION SYSTEM FOR
DEPOSITION OF NANO-SCALE MULTILAYER FILM**

5 Technical Field

The present invention relates to an automatic valve control system in a plasma chemical vapor deposition system or a chemical vapor deposition system for deposition of
10 nano-scale multilayer film, and more particularly, to an automatic valve control system in a plasma chemical vapor deposition system or a chemical vapor deposition system for deposition of nano-scale multilayer film having nano-scale ultra-high hardness and multifunction, by using a plasma
15 chemical vapor deposition method or a chemical vapor deposition method.

Background Art

20 A study on fabrication and commercialization of various vacuum films are being vividly in progress with a help of development of a vacuum technology, one of which is an ultra-lattice or artificial lattice thin-film to be handled in the present invention.

25 An ultra-lattice thin-film is a basic research model for studying an interfacial property between heterogeneous materials, the terminology of which names a multilayer film

in which the thickness of each layer is thin up to a nano-scale degree.

If heterogeneous materials are adjusted in a film thickness direction with a scale nearly close to an interval
5 between the lattices in a crystal existing in the nature, it is meant that they are shown as an artificial one-dimensional lattice.

A model view of an ideal ultra-lattice is illustrated in FIG. 1. In a multilayer thin film in which layers of
10 each micron level are deposited, as shown in FIG. 1, materials A and B have an intrinsic characteristic, respectively, but the whole multilayer film to be expected has a function of a composite material which is obtained by taking an average value or each superior point of the materials A and B.

15 In contrast, an ultra-lattice thin-film where materials A and B are deposited, does not expose inherent properties of the materials A and B, but exhibits a new property as a whole. That is, the ultra-lattice thin-film reveals a new property completely different from the
20 materials A and B.

Even in the result of a study, a cause that an ultra-lattice thin-film reveals a new property, has not been still thoroughly examined, but reported that it should be due to a lattice distortion effect, an interfacial effect,
25 a stratiform structure effect, an artificial periodic effect, etc., between heterogeneous materials.

In the case that an ultra-lattice is applied to a hard

coating, respectively different two metal or ceramic (carbide or nitride) layers are alternately deposited. As a result, movement of the potential in each layer and movement of the potential cross an interlayer interface is suppressed,
5 to accordingly obtain a hardness of 50GPa or more.

Here, in order to effectively suppress movement of the potential, the thickness of each layer should be adjusted up to several nano-meters.

In order to obtain the property of the ultra-lattice
10 thin-film as described above, the thickness of each layer should not only be adjusted, but also a gradient of concentration should not occur due to a diffusion of the heterogeneous materials in an interface. Because of these limitations, the ultra-lattice thin-film has been fabricated
15 up to now, chiefly by using a sputtering device where a substrate is rotatably designed or an evaporation method using two independent evaporation sources.

In the case of the sputtering method, when two different targets are installed so as to face each other, and a substrate
20 is rotated at a constant speed while sputtering, it has been known that the thickness of each layer can be controlled by controlling a rotational speed of the substrate and an intensity of a bias applied to the targets, by use of a property that a corresponding material is chiefly deposited when the
25 substrate reaches the front of each target.

The evaporation method controls evaporation of heterogeneous materials periodically through opening and

closing of a shutter installed in front of the two evaporation sources.

Using the sputtering and evaporation methods allows fabrication of an ultra-lattice thin-film by a comparatively
5 simple method, and enables the thickness of each layer to be easily controlled, but cannot perform deposition of a thin-film with respect to a substrate of a complicated shape because of limitation of a physical vapor deposition.

A chemical vapor deposition (CVD) and a plasma chemical
10 vapor deposition (PECVD) method supplies a reaction material in a gaseous form to perform a deposition process. Taking this into consideration, a study on fabrication of a multilayer thin-film through a control of a mass flow meter (MFC) of gas has been attempted.

15 For example, in order to obtain a multilayer thin-film of TiN and TiCN, a supply of CH₄ gas is controlled through an on/off time control of a mass flow meter (MFC). However, in this case, since it takes about one minute to stabilize an amount of gas through the mass flow meter (MFC), it is
20 not possible to adjust the thickness of each layer into several tens of nanometers or less. Further, in the case that a bubbler or evaporator is used in order to supply a liquid or solid reaction material in a gaseous form, it takes much more time to stabilize an amount of flow. As a
25 consequence, it becomes more difficult to control the thickness of each layer through the mass flow meter.

Disclosure of the Invention

To solve the above problems, it is an object of the present invention to provide an automatic valve control system in a plasma chemical vapor deposition system or chemical vapor deposition system for deposition of a nano-scale multilayer film, in which a supply of a source can be quickly and accurately controlled in order to fabricate an ultra-lattice successfully by using a plasma chemical vapor deposition method or chemical vapor deposition method, and limitation of a substrate shape based on a physical vapor deposition such as a sputtering or evaporation method can be solved in the case that an ultra-lattice thin-film is fabricated by using a plasma chemical vapor deposition method or chemical vapor deposition method.

To accomplish the above object of the present invention, there is provided an automatic valve control system in a plasma chemical vapor deposition system or chemical vapor deposition system for deposition of a nano-scale multilayer film, the automatic valve control system comprising: a chamber in which a multilayer thin-film can be formed of at least two components by using a plasma chemical vapor deposition method or chemical vapor deposition method; at least two source supplies supplying a reaction material including a component constituting any one layer of the multilayer thin-film; at least two paths each whose middle portion is connected to each source supply, whose one end

is connected to the chamber, and whose other end is connected to a bypass tube for controlling an amount of flow; a vacuum pump connected to the bypass tube; and at least four valves installed in either side of each path around each connection
5 portion in each source supply, which is opened or closed.

The valves comprise a solenoid valve which can be automatically opened or closed, respectively. The present invention further comprises a controller controlling opening or closing of the valves with a predetermined interval of
10 time. Thus, the controller controls the valves, and supplies the chamber with materials necessary for forming a thin-film through the at least two paths and source supplies, in a predetermined sequence, in order to form a multilayer thin-film.

15 Also, the present invention further comprises a third source supply in order to smoothly perform a fabrication process, in which a source can be directly supplied to the chamber via the third source supply, in the case of using the source having a component which reacts each other and
20 is hardened during introduction of the source into the chamber among the sources supplied via the at least two source supplies, and a source which forms a plasma continuously stably, among processes is supplied through the third source supply, in the case of the plasma chemical vapor deposition
25 method. The third source supply further comprises a solenoid valve whose opening and closing control can be performed in order to control a source supply.

As described above, the present invention can control a supply of sources smoothly and quickly, and thus can fabricate a nano-scale multilayer thin-film quickly and accurately by using a plasma chemical vapor deposition method or chemical vapor deposition method.

Brief Description of the Drawings

The above and other objects and advantages of the present invention will become more apparent by describing the preferred embodiments thereof in more detail with reference to the accompanying drawings in which:

FIG. 1 is an exemplary view for explaining an ultra-lattice thin-film structure;

FIG. 2 is a configurational view for explaining an automatic valve control system in a plasma chemical vapor deposition system for deposition of a nano-scale multilayer film according to the present invention; and

FIG. 3 is a graphical view showing the hardness of a TiN/AlN ultra-lattice thin-film according to the present invention.

Best Mode for Carrying out the Invention

Hereinbelow, an automatic valve control system in a plasma chemical vapor deposition system or chemical vapor deposition system for deposition of a nano-scale multilayer

film according to the present invention, will be described with reference to the accompanying drawings.

An automatic valve control system used in the present invention is shown in FIG. 2. Here, a reactor of a general plasma chemical vapor deposition system, that is, a chamber 10 is used as it is. Reaction gases to be supplied, that is, a first source 31 and a second source 32 are designed to be supplied to the chamber 10 via a valve system 20.

First to fourth valves 27 to 30 each formed of an air pressure valve are used in the valve system 20. The first to fourth valves 27 to 30 are connected to a solenoid valve (not shown) which can be electrically controlled in order to automatically control on-and-off operations of the first to fourth valves.

The valve system 20 is connected to a first connection tube 21 connected to the chamber 10, and a second tube 24 connected to a second pump 33 to play a role of a bypass tube for bypassing a reaction gas, a first path 22 and a second path 23 connected to the first and second connection tubes 21 and 24 in parallel with each other, respectively, a first source 31 and a second source 32 connected to the middle portions of the first and second paths 22 and 23, receiving a source from first and second sources 31 and 32, respectively, and transferring the received source, and the first to fourth valves 27 to 30 installed along the first and second paths 22 and 23 around the first and second source supplies 25 and 26.

Here, the bypass tube, that is, the second connection tube 24 is essentially required for consistently maintaining an amount of gas during fabrication of a multilayer thin-film. The end of the connection tube 24 is connected to a second
5 pump 33 which operates independently of a first pump 12 which is used in the chamber 10 in order to prevent a back stream of gas to be expected in an entrance portion of the pump.

The chamber 10 is fabricated in a cylindrical shape of 30cm in diameter and 24cm in height, in 304 stainless steel.
10 A plasma generator 17 for generating a plasma is installed in the upper portion of the chamber 10. The plasma generator 17 includes a planar capacitive type electrode, which receives power supplied via a matching unit 40 from a radio frequency (RF) generator 45 and operates.

15 A sample piece 16 to be tested is installed on a table 13 installed in the lower portion of the chamber 10. The sample piece 16 is formed of resistance wires, and is heated up to a set process temperature by a heater 14 generating heat by power supplied by a power source 15.

20 The chamber 10 and the table 14 except for the plasma generator 17 are electrically grounded.

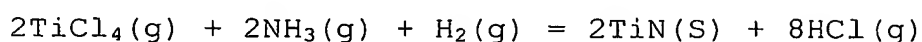
Also, the pressure in the chamber 10 is measured by a thermocouple gauge.

An ultra-lattice thin-film is fabricated with an
25 automatic valve control system according to the present invention in which TiN and AlN are repeatedly deposited in the thickness of a nano-scale unit, respectively. Here,

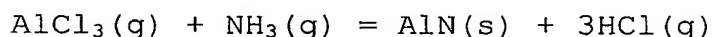
TiCl₄, H₂, or NH₃ are used as a reaction gas for deposition of TiN, and AlCl₃, or NH₃ are used as a reaction gas for deposition of AlN.

The thermodynamic reaction equations are expressed in
5 Reaction Equations 1 and 2, respectively.

<Reaction Equation 1>



10 <Reaction Equation 2>



Since TiCl₄ and AlCl₃ exist in liquid and solid states, respectively, it is introduced into the chamber 10 through
15 a bubbling reaction with a carrier gas in an evaporator. Ar and H₂ are used as a carrier gas, respectively. Also, when AlN is deposited, Ar is additionally supplied in order to help activation of plasma.

An amount of each gas is consistently maintained by using
20 a mass flow meter (MFC). The amount of the reaction gas introduced by the bubbling reaction is adjusted by the following principle.

In general, the following Equations 1 and 2 are established among an amount Q_{car} of a carrier gas, an amount
25 Q_{rxn} of a reaction gas introduced into a reaction chamber by a bubbling reaction, a pressure P_{car} of a carrier gas, and a vaporized pressure P_{rxn} of a reaction gas.

<Equation 1>

$$Q_{rxn} = \frac{P_{rxn}}{P_{car} + P_{rxn}} \times Q_{car} = \frac{P_{rxn}}{P_T} \times Q_{car}$$

<Equation 2>

$$P_T = P_{car} + P_{rxn}$$

5 Here, PT can be confirmed by using a pressure gauge
attached to an evaporator. If a pressure of the evaporator
is consistently maintained, an amount of a reaction gas
introduced into a reaction chamber is a function of an amount
of a carrier gas introduced into the evaporator and an
10 evaporation pressure of the reaction gas. When the pressure
and temperature of $TiCl_4$ and $AlCl_3$ are the mercuric evaporation
pressure (mmHg) and the absolute temperature (. K), each
evaporation pressure P is expressed as the following
Equations 3 and 4.

15 <Equation 3>

$$P_{TiCl_4} = \frac{-6360}{T} + 9.66 \log T - 6.12 \times 10^{-3} T$$

<Equation 4>

$$P_{AlCl_3} = \frac{-2919}{T} + 25.129 - 5.788 \log T$$

20 Thus, the evaporation pressure of $TiCl_4$ and $AlCl_3$ is

a function of only temperature. Accordingly, an amount of the reaction gas can be adjusted by controlling the temperature of the evaporator and the amount of the carrier gas, respectively.

5 Meanwhile, NH_3 reacts with a gas of TiCl_4 or AlCl_3 at a low temperature and forms a solid compound such as $\text{TiCl}_4 \cdot n\text{NH}_3$, $\text{AlCl}_3 \cdot n\text{NH}_3$ or NH_4Cl , to thus clog an inflow gas tube. To prevent this, the solid compound is made to be uniformly distributed and introduced via a number of small holes 18
10 formed on an electrode plate formed in the plasma generator 17 installed in the chamber 10. A third source supply tube 35 is connected between a third source 34 such as NH_3 and the chamber 10, and the third source supply tube 35 is opened and closed by a fifth valve 36 formed of a solenoid valve.

15 The plasma generator 17 is formed of a circular plate. The reaction gases supplied from the first and second sources 31 and 32 to the chamber 10, that is, the gases of TiCl_4 and AlCl_3 are made to be uniformly introduced by using a ring type gas distributor 19 installed between the plasma
20 generator 17 and the sample piece 16.

Based on the above description, the sources 1 and 2 used in the present invention are summarized as follows with reference to FIG. 2.

Source 1: TiCl_4 , Ar, H_2

25 Source 2: AlCl_3 , Ar, H_2

Process conditions of TiN/AlN ultra-lattice thin-film is shown in the following Table 1.

[Table 1]

Process conditions of TiN/AlN ultra-lattice thin-film

	TiN	AlN
Reaction gas and flow amount	TiCl ₄ : 1.4sccm	AlCl ₃ : 1.9sccm
	H ₂ : 100sccm	H ₂ : 100sccm
	Ar : 40sccm	Ar : 40sccm
	NH ₃ : 20sccm	
Process temperature	530℃	
RF power	50W	
Total thickness of deposition film	2~3μm	

5

The first and second pumps 12 and 33 are formed of a mechanical rotary pump, respectively. The RF generator 45 is formed of a radio frequency generator of 13.56MHz. The matching unit 40 is made of an impedance matching box of a capacitive type.

10

The TiN/AlN ultra-lattice thin-film fabricated according to the present invention has been fabricated by the following set of sequences.

15

Sequence 1.

TiCl₄ and AlCl₃ supplied through the evaporator and the reaction gases Ar and H₂ are discharged via the second pump 33 connected to the second connection tube 24, in order
5 to stabilize an amount of gas.

Sequence 2.

If an amount of all reaction gases is stabilized, NH₃ is made to be introduced into the chamber 10 via a small hole
10 on the upper electrode plate which is the plasma generator 17, to thereby form a plasma.

Sequence 3.

If the plasma is stabilized, the first valve 27 is opened
15 and the third valve 29 is closed, for deposition of TiN. Accordingly, the reaction materials for deposition of TiN, that is, TiCl₄, H₂, and NH₃ are introduced into the chamber 10. Here, the fourth valve 30 is opened, to thereby discharge the reaction material for deposition of AlN, that is, AlCl₃
20 and NH₃ by the second pump 33 so that the amount of flow does not change.

Sequence 4.

If deposition of TiN is completed, the first valve 27
25 is closed and the third valve 29 is opened until the reaction material such as TiCl₄ remaining in the chamber 10 is completely discharged (this process is necessary to obtain a clean

interface by preventing a Ti concentration gradient in the interface between TiN and AlN which can be expected in advance, in the case that the reaction gas for deposition of AlN is introduced. In the present invention, it takes about 10
5 seconds.) .

Sequence 5.

Then, the second valve 28 is opened and the fourth valve 30 is closed, to make the reaction gases for deposition to
10 be introduced into the chamber 10. Here, the third valve 29 is opened so that an amount of TiCl_4 is consistently maintained.

Sequence 6.

By repeating the sequence 4, a residual gas such as AlCl_3
15 remaining in the chamber 10 is removed.

The on-and-off state of each valve for the above-described sequences is shown in the following Table
2.

20

25

[Table 2]

The on-and-off state of each valve for the processing sequences

Sequence	Chamber status	On-and-off state of valves				
		1 st valve		3 rd valve		5 th valve
Sequence 1	Stable flow amount of reaction gas	off	off	on	on	off
Sequence 2	Plasma formation	off		on		on
Sequence 3	TiN deposition	on	off	off	on	on
Sequence 4	Interface standstill	off	off	on	on	on
Sequence 5	AlN deposition	off	on	on	off	on
Sequence 6	Interface standstill	off		on		on

5 By repeatedly performing the sequences 3 through 6, an ultra-lattice TiN/AlN can be effectively grown. Here, the thickness of each layer is controlled by altering a deposition time (sequences 4 and 6) from a growing speed of a mono-layer thin-film of TiN and AlN obtained through a preliminary
 10 experiment. In order to grow an ultra-lattice thin-film of 2~3 μ m in thickness necessary for application to a hard thin

film, a process of repeating the sequences 3 through 6 by 300~500 times or so.

The opening and closing control of each valve is automatically controlled by supplying an electrical signal to a solenoid valve connected to the first to fourth valves 5 27 to 30 through a computer program.

The ultra-lattice thin-film of TiN/AlN fabricated by the above-described processes is examined into a transmission electron microscopy picture. A sample piece observed through 10 an electron microscopy is shown into a pattern shown in FIG. 1, in which a bilayer period shows up over about 5nm.

That is, a bright portion represents a TiN layer, and a dark portion represents an AlN layer. Here, a bilayer period means an addition of the thickness of a layer of TiN and that 15 of a layer of AlN. The thickness of the ultra-lattice thin-film fabricated in the present invention is controlled within several nano-meters.

Meanwhile, a change in the hardness of a multilayer of TiN/AlN fabricated according to the present invention is 20 examined. As shown in FIG. 3, when the repetition period of a multilayer thin-film is about 5nm, the multilayer thin-film reveals the maximum hardness of 5000 (HK0.01) or higher. Considering that the hardness of the TiN and AlN mono-layer thin-films fabricated by the existing plasma 25 chemical vapor deposition method are 2500 (HK0.01) and 1200 (HK0.01), respectively, the TiN/AlN multilayer thin-film fabricated according to the present invention reveals the

characteristic of an ultra-lattice thin-film.

Industrial Applicability

5 As described above, the present invention can fabricate a nano-scale multilayer thin-film representing the characteristic of the ultra-lattice thin-film through a plasma chemical vapor deposition method without causing an amount of the reaction gas to be changed. Also, the present
10 invention can solve the shortcomings of a physical vapor deposition (PVD) method such as a sputtering method, which is a very epoch-making invention in that the present invention provides a new method of fabricating an ultra-lattice thin-film.

15 As described above, the present invention has been described with respect to particularly preferred embodiments. However, the present invention is not limited to the above embodiments, and it is possible for one who has an ordinary skill in the art to make various modifications and variations,
20 without departing off the spirit of the present invention.

What is claimed is:

1. An automatic valve control system in a plasma chemical vapor deposition system or chemical vapor deposition system for deposition of a nano-scale multilayer film, the automatic valve control system comprising:

a chamber in which a multilayer thin-film can be formed of at least two components by using a plasma chemical vapor deposition method or chemical vapor deposition method;

at least two source supplies supplying a reaction material including a component constituting any one layer of the multilayer thin-film;

at least two paths each whose middle portion is connected to each source supply, whose one end is connected to the chamber, and whose other end is connected to a bypass tube for controlling an amount of flow;

a vacuum pump connected to the bypass tube; and

at least four valves installed in either side of each path around each connection portion in each source supply, which is opened or closed.

2. The automatic valve control system in a plasma chemical vapor deposition system or chemical vapor deposition system of claim 1, wherein said at least four valves comprise a solenoid valve which can be automatically opened or closed, respectively.

3. The automatic valve control system in a plasma chemical vapor deposition system or chemical vapor deposition system of claim 1, further comprising a third source supply for directly supplying the source having a component which reacts each other and is hardened, to the chamber, during introduction of the source into the chamber among the sources supplied via the at least two source supplies.

4. The automatic valve control system in a plasma chemical vapor deposition system or chemical vapor deposition system of claim 3, wherein said source supply further comprises a solenoid valve which can be automatically opened or closed.

5. The automatic valve control system in a plasma chemical vapor deposition system or chemical vapor deposition system of any one of claims 1, 2 and 4, further comprising a controller controlling opening or closing of the valves with a predetermined interval of time.

6. The automatic valve control system in a plasma chemical vapor deposition system or chemical vapor deposition system of claim 5, wherein said controller controls the valves, and supplies the chamber with materials necessary for forming a thin-film through the at least two paths and source supplies, in a predetermined sequence, in

order to form a multilayer thin-film.

7. The automatic valve control system in a plasma
chemical vapor deposition system or chemical vapor
5 deposition system of claim 1, wherein said chamber further
comprises a gas distributor connected to one end of the path
and installed in the chamber, for uniformly distributing
the sources.

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FIG. 1

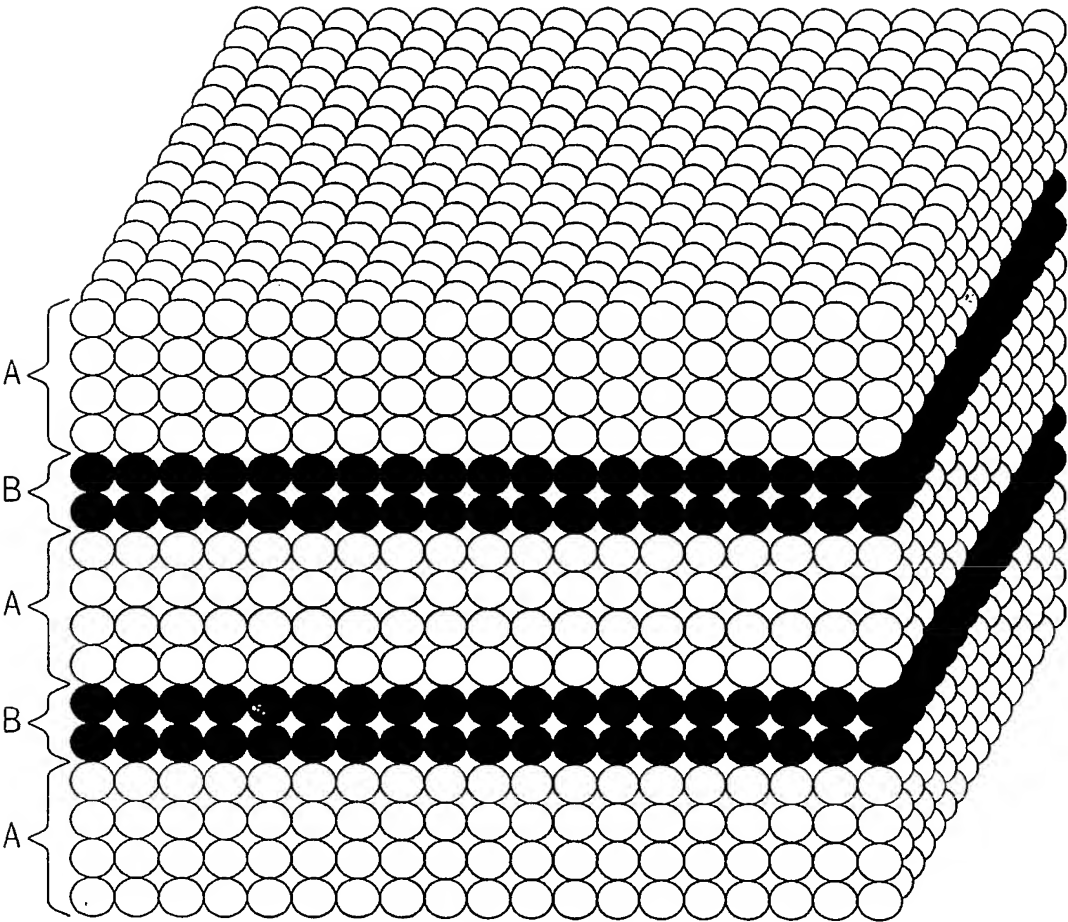
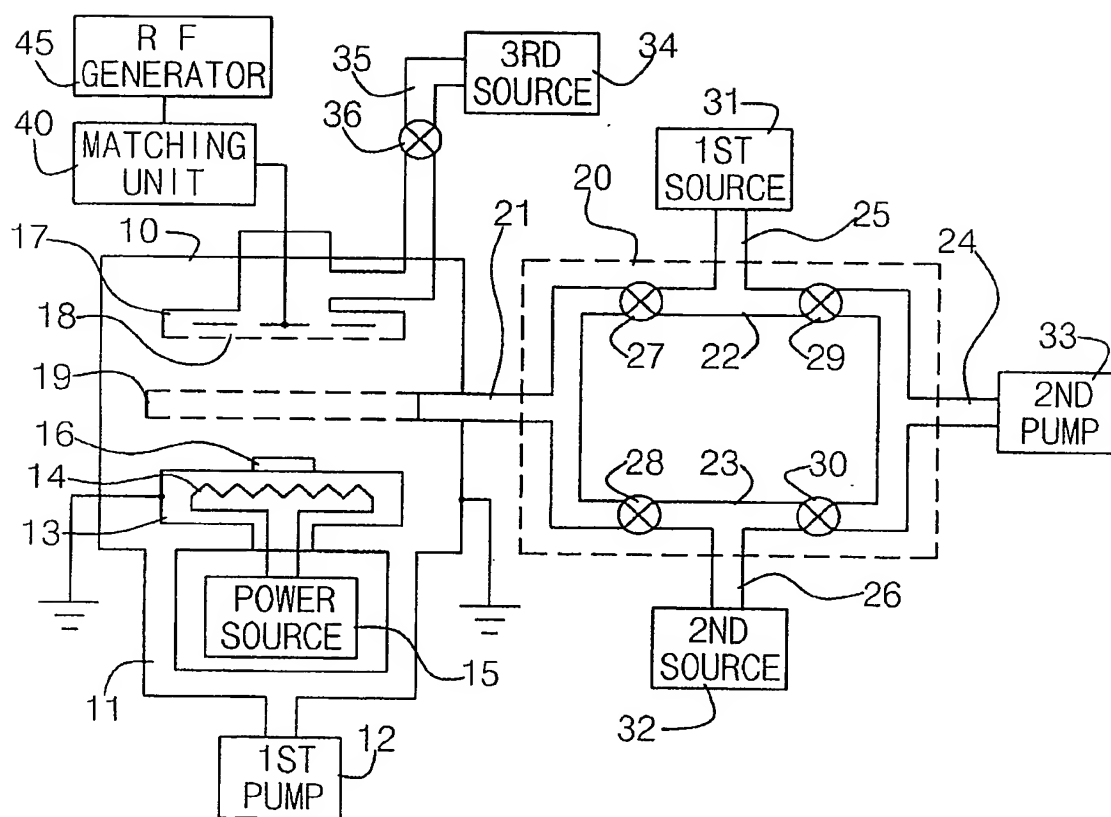
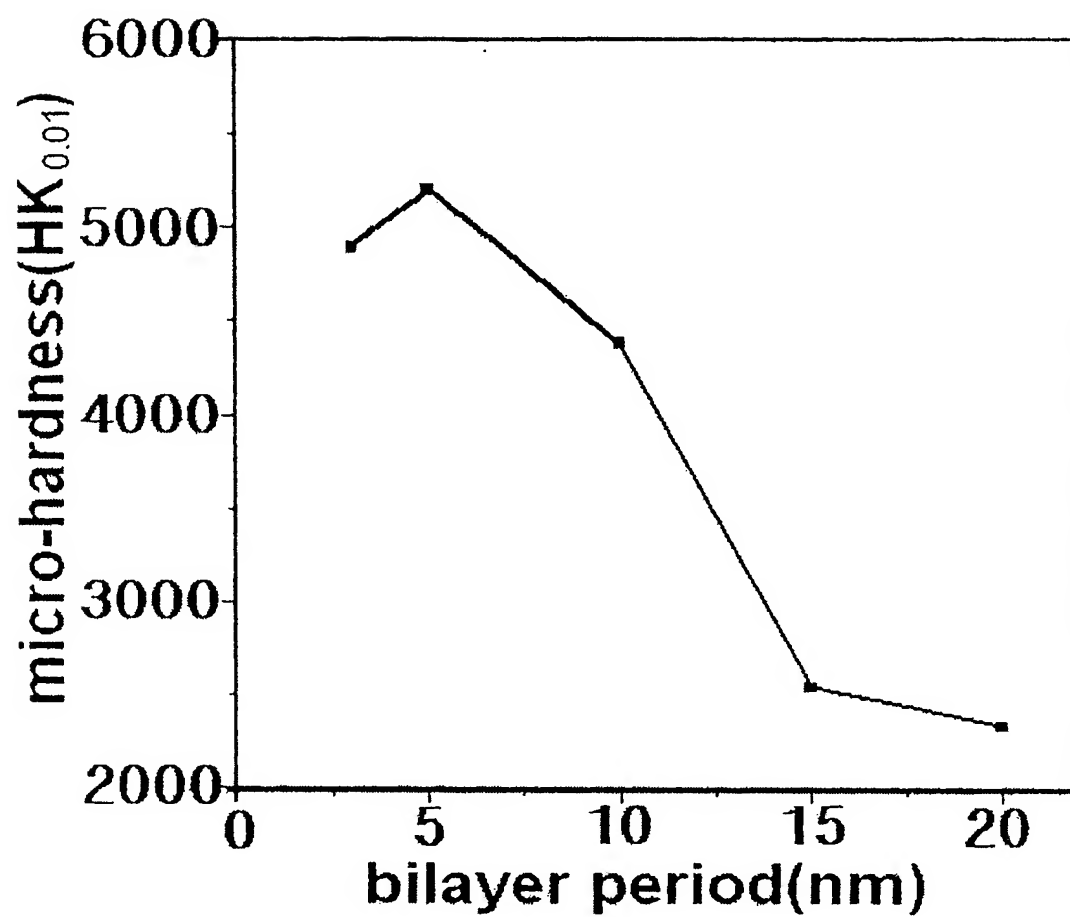


FIG. 2



3/3

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR03/00689

A. CLASSIFICATION OF SUBJECT MATTER**IPC7 C23C 16/455**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,562,776 A (ENERGY CONVERSION DEVICES INC.) 08 October Abstract and Figure 1.	1-4
A	JP 02-243504 (KOBESTEEL LTD.) 29 September 1990 Claim 1 and Figure 1.	1-4
A	JP 12-144429 (FUJIELECTRIC CO, LTD.) 26 May 2000 Claims and Figure 2.	5-6
A	JP 10-190074 (KOMATSU LTD.) 21 July 1998 Claim 1 and Figure 1.	7

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

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Date of mailing of the international search report

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